

# ENVIRONMENTAL PROTECTION

UDC 691.4:628.54.004.8

## UTILIZATION OF WASTEWATER PRECIPITATES FROM TANNERIES IN PRODUCTION OF CONSTRUCTION CERAMICS

A. V. Belyakov,<sup>1</sup> S. A. Komissarov,<sup>1</sup> and T. M. Korchuganova<sup>1</sup>Translated from *Steklo i Keramika*, No. 3, pp. 3 – 6, March, 1998.

Ceramic samples were obtained from the mixtures containing sewage precipitate from Ryazan' Tannery, clay from a local brick factory, and basic slag from Ryazan' Metallurgical Plant. The sample properties (compressive strength, acid resistance, and alkali resistance) as well as the presence of heavy metals in the solutions after testing were determined. The mixtures containing the precipitate reliably bind heavy metals and are promising for utilization of tannery waste in production of ceramic wall materials. The processes occurring in sintering of the samples are explained.

The tanning and leather industry generates a substantial amount of waste which pollutes the environment. Soluble chromium compounds are the most dangerous since chromium extract (solution of basic chromium sulfates) is usually used in the chrome tanning process. Structural ceramics technology provides the possibility of converting soluble chromium compounds into the insoluble form. The chromium will be bound in silicates, aluminosilicates, and vitreous phase that are resistant to water and to acid and alkaline aqueous solutions.

In the course of processing leather, both organic and inorganic materials end up in the waste. The inorganic reactants are applied in different technological phases and a substantial portion enters the sewage and after treatment of the sewage, ends up in the sewage precipitate. Table 1 displays the material balance of the chemicals used in production of tanned leather [1].

Sewage precipitate is a combination of chemical and excessive biological sludge. The precipitate contains fat and meat pieces, hide shreds, blood clots, hair and bristle, earth, sand, inhibitors, fats, soluble proteins, as well as antiseptics and sharpeners used for soaking (surfactants, sulfides, sulfates etc.) and protein organic substances which are instrumental in rotting of sewage liquid. In addition, the precipitate contains numerous bacteria some of which are pathogenic [2].

The chemical analysis of the sewage precipitate at the Ryazan' Tannery showed its content to be as follows (hence-

forth wt.% is indicated): 2.0 inorganic substances (converted into chemical elements), 40.0 water, and 58.8 organic compounds of which 19.8% are fats. The mineral part of the sludge is mostly represented by compounds containing calcium, magnesium, silicon, iron, aluminum, manganese, and chromium. The prevalence of calcium (up to 19%) is determined by the liming technology and the prevalence of chromium (up to 12.3%) is determined by the chrome tanning technology and incomplete purification of sewage water that causes chromium to pass into the precipitate.

On incineration of the sewage precipitate at the Ryazan' tannery in a rotating furnace using natural gas as a fuel at 950°C, the resulting ash had the following content (%). 1.0 water, 11.0 chromium salts including 8.7 chromium (III) and 2.3 chromium (VI); 29.0 calcium and magnesium; 1.8 chlorides; 4.5 sulfides and the pH of a 1-% aqueous solution was 11.5. The apparent density was 0.75 g/cm<sup>3</sup> [3].

Considering that the waste precipitate is large-tonnage waste, to save transport costs it ought to be processed in the neighborhood. Therefore, the clay used for brick production at a local brick factory was selected for the experiments. The calcination loss for this clay amounted to 2.2%. The initial moisture of the clay sample analyzed was 16.5%. The drying sensitivity coefficient determined by A. F. Chizhsky's method [4] was 1.18%. Thus, this clay belongs to clays with low drying sensitivity. On firing, the metals contained in the precipitate (above all, the chrome) should be bound into silicates, aluminosilicates, and vitreous phase.

The cations Cl<sup>-</sup>, S<sup>2-</sup>, SO<sub>4</sub><sup>2-</sup>, and others are found in the precipitate. In order to bind them we tried to use the main

<sup>1</sup> D. I. Mendeleev Russian Chemical Engineering University;  
Russian Correspondence Course Institute of Textile and Light Industry.

slag from the Ryazan' Metallurgical Plant. It was assumed that on firing, the calcium oxide contained in the slag will facilitate binding of the anions into low-solubility solid solutions or vitreous phase. The assumption was based on the data on the chemical composition of the ash resulting from incineration of the precipitate. The ash had a clearly basic character ( $\text{pH} = 11.5$ ) and the anions were preserved.

The samples were made of clay of 16.5% moisture and slag of 9.4% moisture. The precipitate and slag were added to clay above 100%. Water was introduced in the amount necessary for good moldability. The mixture was mixed thoroughly by hand and then the samples were molded plastically. The compositions of the molding mixtures are given in Table 2. The compositions in Series 1 contained clay and precipitate, and those in Series 2 contained clay, precipitate, and slag.

With an increase in the amount of precipitate introduced, the plasticity and moldability of the molding mixtures improved. Each composition was used to make 10 samples measuring  $50 \times 25 \times 5$  mm. The samples were dried naturally at  $20^\circ\text{C}$  for 3 days and then dried at  $100 - 110^\circ\text{C}$  until the mass became constant and fired at  $950$ ,  $100$ , and  $1050^\circ\text{C}$  in air. Firing was carried out according to the fire shrinkage determination method in [4]. The entire set of samples was placed in the furnace, heated to  $950^\circ\text{C}$ , cured for 30 min, then some samples were transferred to a neighbouring furnace at a temperature of  $800^\circ\text{C}$  while the temperature in the first furnace was raised to  $1000^\circ\text{C}$  and the whole procedure was repeated. After the end of curing at  $1050^\circ\text{C}$ , both furnaces were switched off simultaneously. The open porosity and average density were determined by the hydrostatic weighing method.

The chemical stability of the samples obtained was determined by the action of acid (GOST 473.1-81) and alkaline (GOST 473.2-81) media.

The physicochemical and physicochemical properties of the samples were determined as well. Depending on the precipitate content, the color of the sample after firing varied from orange (pure clay) to dark-brown. The properties of series 1 samples are shown in Table 3, and those of series 2 samples are shown in Table 4.

It can be seen that the air shrinkage of all samples exceeds the fire shrinkage. The fire shrinkage varies little upon introduction of the precipitate in the mixture and is equal to nearly 2%. The air shrinkage decreases significantly upon addition of the precipitate to the mixture. This may be due to the fact that the precipitate acts as a leaning component, impeding air shrinkage. The presence of hair residues in the sludge ought to contribute to a decrease in the shrinkage. As the precipitate content increases from 10 to 30%, the air shrinkage increases at the expense of the precipitate shrinkage. As the precipitate content grows from 30 to 40%, the air shrinkage decreases again. Introduction of the precipitate improves the moldability of the mixture since the substances it contains act as surfactants.

The samples were molded without adding water (Table 2). Perhaps with an increase in the precipitate content from 30 to 40%, the samples become denser since in the course of molding, partial squeezing of water out of the mixture was observed. Besides, it may be related to insufficient homogenization of the mixtures and formation of a clay-enriched "skeleton" that has a low shrinkage.

In the samples with slag impurity the fire shrinkage was 2-3%. The slag and precipitate acted as leaning components which reduced the shrinkage of these samples compared to the pure clay samples. The samples of compositions 6 and 7 containing a substantial amount of the precipitate had air shrinkage of about 6%. The shrinkage was determined by the substantial precipitate and water content. A further in-

TABLE 1

Process	Chemical material	Content, %	Non-reacting part of the amount used, %
Conservation	NaCl	40*	100**
Liming-dehairing	$\text{Ca}(\text{OH})_2$	4.5*	75
	$\text{Na}_2\text{S}$	3*	73
Deliming	$(\text{NH}_4)_2\text{SO}_4$	1.5***	80
Pickling-tanning	NaCl	4***	90
	$\text{Ca}(\text{HCOO})_2$	1***	—
	$\text{H}_2\text{SO}_4$	1.2***	80
	$\text{Cr}_2\text{O}_3$ ****	2***	25
	$\text{Na}_2\text{CO}_3$	0.3***	—

\* Of the fresh material mass.

\*\* Including 30% in soaking.

\*\*\* Of the depilated hide mass.

\*\*\*\* Chrome compounds converted into  $\text{Cr}_2\text{O}_3$ .

TABLE 2

Composition	Content, wt. %			
	clay	precipitate	slag	water
<i>Compositions of Series 1</i>				
1	100	—	—	17.5
2	100	10	—	15.4
3	100	20	—	13.0
4	100	30	—	11.0
5	100	40	—	—
<i>Compositions of Series 2</i>				
6	100	60	—	10.0
7	100	40	20	13.0
8	100	30	30	13.5
9	100	20	40	15.0
10	100	10	50	18.5
11	100	—	60	23.8

crease in the slag content at the expense of a decrease in precipitate content resulted in the decreased air shrinkage.

With an increase in the precipitate content in the mixture, the open porosity of the fired samples grew from 20 to 33%, as could be expected (Table 3). An increase in the precipitate content to 60% (Table 2, composition 6) caused an increase in the open porosity to 41 % (Table 4). Accordingly, with an increase in the open porosity, a decrease in density was observed. The density of the samples decreased from 2.01 g/cm<sup>3</sup> (pure clay) to 1.24 g/cm<sup>3</sup> (mixture with 60% precipitate content). Partial substitution of slag for the precipitate produced a decrease in the open porosity from 40 to 29% and increase in the density from 1.2 to 2.1 g/cm<sup>3</sup> (Table 4).

The increase in porosity related to the increase in the precipitate content in the mixture caused a decrease in the compressive strength of the samples (Table 3). With the precipitate content increasing to 30%, the strength of the samples decreased and then increased slightly. It can be explained by the insufficient homogeneity of the clay-enriched "skeleton". The presence of a stronger "skeleton" may lead to an increase in the strength of the samples.

Partial replacement of the precipitate with slag (Table 2) did not cause a regular decrease in the strength with the the observed decrease in porosity. This is related to significant modification of the chemical composition and, accordingly, the structure of the samples in substitution of slag for precipitate. A slight increase in the compressive strength was recorded for samples of compositions 9 and 11. A sharp drop

in strength began upon introduction of 10% precipitate, which cannot be explained just by increased porosity. It may be related to the formation of dicalcium silicate from the calcium oxide contained in the precipitate and SiO<sub>2</sub> from the clay. It is known that dicalcium silicate is primarily formed in the reaction of calcium and silicon oxides. The salts contained in the precipitate probably acted as fluxes facilitating the synthesis of dicalcium silicate and conversion of silicon dioxide from  $\alpha$ -quartz into  $\alpha$ -cristobalite. The formation of dicalcium silicate and  $\alpha$ -cristobalite is associated with a significant increase in volume, which agrees well with the low fire shrinkage of the samples.

The increase in volume may be the reason for the emergence of microcracks and the decrease in the strength of the samples. The polymorphous transitions in dicalcium silicate from the  $\beta$ -form to the  $\gamma$ -form, and in cristobalite from the  $\alpha$ -form to the  $\beta$ -form may also be the reason for the appearance of microcracks and the sharp decrease in strength. The noticeable decrease in strength with an increase in the temperature and cure duration is probably related to an increase in the quantity of the emerging dicalcium silicate and  $\alpha$ -cristobalite. A decrease in strength was observed both in the pure clay samples and in the samples containing slag and precipitate. In the latter samples, the variation in strength was more evident due to the presence of fluxes.

With an increase in the firing temperature, the alkali resistance of samples of series 1 and 2 decreased for all compositions (Tables 3 and 4). The acid resistance of mixtures

TABLE 3

Parameter	Firing temperature, °C	Samples of series 1				
		1	2	3	4	5
Air shrinkage, %		7.0	2.2	9.3	14.4	2.7
Fire shrinkage, % /total shrinkage, %	950	2.0/9.0	0.6/2.8	2.0/11.3	1.7/16.1	2.0/4.7
	1000	2.0/9.0	1.7/2.9	2.1/11.4	1.7/16.1	2.0/4.7
	1050	2.0/9.0	1.7/2.9	2.1/11.4	1.7/16.1	2.0/4.7
Open porosity, %	950	20.0	26.6	27.6	29.2	31.7
	1000	23.4	26.3	28.8	30.6	33.0
	1050	20.4	25.2	27.6	29.6	32.5
Density, g/cm <sup>3</sup>	950	2.04	1.95	1.94	1.93	1.72
	1000	2.01	1.95	1.93	1.92	1.72
	1050	2.02	1.95	1.93	1.92	1.72
Compressive strength, MPa	950	20.6	3.7	3.2	2.0	4.3
	1000	21.6	3.3	2.7	2.5	2.3
	1050	20.8	6.8	3.3	2.3	4.8
Acid resistance, %	950	97.3	91.5	93.9	94.1	95.1
	1000	96.2	93.2	92.2	93.5	93.6
	1050	96.2	93.2	90.2	93.0	91.9
Alkali resistance, %	950	94.0	98.5	99.6	94.5	92.0
	1000	93.8	98.1	97.9	93.5	87.4
	1050	92.2	97.8	96.0	93.0	83.1

containing only clay and precipitate also decreased with an increase in the firing temperature. It may be related to the appearance of microcracks owing to the polymorphous conversions in dicalcium silicate and silicon dioxide and agrees with the modification in strength and density. The exceptions were samples of compositions 2, 8, and 9 which exhibited increased acid resistance with an increase in the firing temperature.

The introduction of the base precipitate in the clay resulted in a noticeable increase in the alkali resistance and a decrease in the acid resistance for samples of compositions 1 and 2. A further increase in the precipitate content in the compositions of series 1 produced a decrease in the alkali resistance. The acid resistance of the samples fired at 950°C increased with an increase in the precipitate content (Table 3) and at 1000 and 1050°C this regularity disappeared.

The chemical resistance is related to the porosity, i.e., to the shape and size distribution of the pores and to the substances on the pore surface. The pore structure depends on the amount of precipitate and slag added to the clay, and the microcracks depend on the resulting amount of dicalcium silicate and  $\alpha$ -cristobalite. The chemical composition of the pore surface depends on the quantities and types of impurities. In firing, cations of variable valence are reduced, including reduction of  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$  under the action of the reducing agent from the carbon monoxide and carbon resulting from the burning up of the organic part of the precipitate. This process is facilitated by the presence of acid oxides, above all silicon oxide. At the same time, under heat treatment the reverse transition of the ion  $\text{Cr}^{3+}$  to  $\text{Cr}^{6+}$  is also possible in the presence of basic cation (of alkali and alkaline-earth metals). These cations are present in the precipitate and the slag. The silicates formed on the surface of the pores have low acid resistance and relatively high alkali resistance.

The main purpose of the present experiment was conversion of heavy metals, primarily chromium, into insoluble form. The qualitative determination of chromium was carried out using acid-alkali and hydrosulfide methods. In addition, the salts of heavy metals were identified by the fractional method and emission spectral analysis. For this purpose the fired samples were held in distilled water, 80% acetic acid, and 30% alkali solution (NaOH) for 2 h while boiling. The extracts obtained were analyzed by the methods listed above.

The concentrations of the washed off components of series 1 samples in the form of ions in aqueous, acetic acid and alkaline solutions as well as those of series 2 samples in aqueous solutions were insufficient for qualitative identification using the alkali-acid and hydrogen sulfide methods. The data obtained indicate that the ceramic materials of series 1 (clay and sewage precipitate) are environmentally safe.

In the analysis of the components of series 2 samples washed off with acetic acid and alkaline solutions, the qualitative reactions based on the hydrogen sulfide method yielded positive results regarding the cations of the third analytical:  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ . Taking into account the solubility product values, it can be stated that the concentration of  $\text{Cr}^{3+}$  ions exceeded  $1.35 \times 10^{-14}$  mole/liter, that of  $\text{Mn}^{2+}$  exceeded  $3.74 \times 10^{-14}$ ,  $\text{Ni}^{2+}$  exceeded  $5.48 \times 10^{-17}$  and  $\text{Zn}^{2+}$  exceeded  $2.83 \times 10^{-19}$  mole/liter.

The experiments revealed that addition of the precipitate to clay makes it possible to bind reliably heavy metals, above all chromium. The concentration of these metals in aqueous, acid and alkali extracts was significantly below the maximum permissible values.

The ceramic thus obtained has good prospects for being used as heat-insulating material for inside walls. This ceramic has a higher porosity and, accordingly, a lower average density and thermal conductivity and better sound-insulating

TABLE 4

Parameter	Firing temperature, °C	Samples of series 2					
		6	7	8	9	10	11
Air shrinkage, %	—	6.0	6.0	7.1	3.2	3.9	3.2
Fire shrinkage, % / total shrinkage, %	1000	2.0/8.0	1.5/7.5	2.0/9.1	2.9/6.1	2.0/5.9	2.2/5.4
	1050	2.0/8.0	2.0/8.0	2.0/9.1	2.4/5.6	2.0/5.9	2.7/5.9
Open porosity, %	1000	40.7	38.2	36.2	34.0	32.7	29.1
	1050	41.5	40.0	37.8	35.2	33.1	29.3
Density, g/cm <sup>3</sup>	1000	1.32	1.48	1.71	1.80	1.90	2.12
	1050	1.24	1.49	1.60	1.93	1.84	1.91
Compressive strength, MPa	1000	1.4	1.8	2.6	3.1	2.1	2.3
	1050	0.7	0.6	1.0	0.9	0.5	1.2
Acid resistance, %	1000	93.8	94.4	88.3	76.7	99.3	97.1
	1050	90.9	92.6	93.2	94.6	92.6	92.9
Alkali resistance, %	1000	99.9	99.9	99.8	99.7	99.4	99.9
	1050	90.7	88.0	90.7	95.3	96.0	92.8

capacity than clay bricks. These properties can be varied depending on the amount of precipitate introduced. The organic compounds contained in the precipitate act as surface-active substances and facilitate molding and subsequent drying. On firing, the heat arising from oxidation of organic compounds is used for heating the samples, and the reducing agent emerging inside the pores facilitates reduction of chromium to a less soluble and safer degree of oxidation (III). The strength of the ceramic is not high, but it can probably be enhanced by increasing the duration of firing. In order to assess the possibility of using this ceramic for outer wall brickwork, its frost resistance ought to be determined.

Addition of the basic slag probably resulted in the fact that part of the chromium was converted to oxidation degree (IV) or retained this degree, which increased the solubility of the chromium, especially in the acid and alkaline environment. Under these conditions, the increase in binding of  $\text{Cl}^-$ ,  $\text{S}^{2-}$ ,  $\text{SO}_4^{2-}$  and other anions does not play a significant role. For binding heavy metals, it is advisable to use a mixture of sewage precipitate with clay. In the clay-precipitate mixtures,

chlorine and sulfur compounds will volatilize and pollute the environment. At present methods for capturing sulfur and chlorine compounds in filters with respective adsorbents are being developed [5, 6].

## REFERENCES

1. P. M. Nacheva, *Development of a Scheme of Highly Concentrated Sulfide-Containing Tannery Waste Sewage, Author's Abstract of Candidate Thesis* [in Russian], Moscow (1989).
2. V. N. Shcherbakov, *Purification and Multiple Use of Sewage Waste Water after Liming of Hides at Tanneries, Author's Abstract of Candidate Thesis* [in Russian], Moscow (1984).
3. V. N. Tkachenko, "Utilization of waste from tannery production," *Kozhevenno-Obuvnaya Promyshlennost'*, No. 10, 9 – 13 (1989).
4. E. S. Lukin and N. T. Andrianov, *Technical Control of Ceramic Production*, Stroiizdat, Moscow (1986).
5. S. P. Sivkov and O. V. Chepovaya, "Highly active adsorbents based on  $\text{Ca}(\text{OH})_2$ ," *Zh. Prikl. Khim.*, **69**(5), 858 – 860 (1996).
6. O. V. Chepovaya, *Production of Adsorbents for Purification of Industrial Gases Based on Power Plant Cinders, Author's Abstract of Candidate Thesis* [in Russian], Moscow (1997).